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Report No. 8926-109

Material - Adhesives - Ceramic - High Temperature Development And Evaluation Study

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Development And Evaluation Study

Abstract

Investigation to develop and evaluate ceramic adhesives for bonding metallic alloys - particularly Armco 17-7 PH stainless steel - at firing temperature of 1450°F or less was conducted. Eleven ceramic adhesive frits were formulated for the application, and examined for melting, flow and strength characteristics. Lap shear strengths of 700 psi at room temperature and 900 to 3200 psi at 800°F were developed in the adhesives studied.

Reference: Pratt, D. S., Shoffner, J. E., Turner, H. C., "Development and Evaluation of High Temperature Ceramic Adhesives," General Dynamics/Convair Report MP 59-110, San Diego, California, 29 March 1960. (Reference attached.)

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A DIVISION OF GENERAL DYNAMICS CORPORATION

SAN DIEGO

REPORT MP-59-110

DATE 29 March 1960

MODEL REA 8011

TITLE

REPORT NO. MP-59-110

DEVELOPMENT & EVALUATION
OF
HIGH TEMPERATURE CERAMIC ADHESIVES

REA 8011

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Authors: Pratt, D. S., Shoffner, J. E., Turner, H. C.
Report No: 8926-109 Date: 29 March 1960
Contract: R.E.A. 8011
Contractor: General Dynamics/Convair
ABSTRACT: Investigation to develop and evaluate ceramic adhesives for bonding metallic alloys - particularly Armco 17-7 PH stainless steel - at firing temperature of 1450°F or less was conducted. Eleven ceramic adhesive frits were formulated for the application, and examined for melting, flow and strength characteristics. Lap shear strengths of 700 psi at room temperature and 900 to 3200 psi at 800°F were developed in the adhesives studied.

30 pages, 5 tables, 11 figures, 2 references.

INTRODUCTION:

The present method of bonding stainless steel honeycomb panels - brazing - is expensive and has made necessary the investigation of other methods of bonding. The inorganic ceramic adhesive offers the advantage of potential lower cost, inertness, lower adhesive weight, lower thermal conductivity, and the absence of galvanic corrosion coupling.

High temperature ceramic adhesives might be developed from one of the following systems:

1. Glass Compositions

   Glass forming materials, i.e., alkalies, alumina, silica, phosphates and others can be blended to form a multitude of physical properties.

2. Glass Compositions Plus Metal Additions

   The addition of finely powdered metals to glass compositions is a recognized method of improving the adhesion of glass to metal.

3. Glass Compositions Plus Recrystallization Products

   The control of the composition, and the rate of cooling can produce recrystallization products in glass. This new crystal growth would change the nature of the system into a complex glass-crystalline grouping with a higher melting point.

4. Glass Compositions Plus Refractory Additions

   Refractory additions, i.e., Al_2O_3, $ZrSiO_4$ or ZrO_2 crystalline formations would resist flowing or shearing at elevated temperatures and thus increase the tensile shear strength of the adhesive.

This limited investigation was conducted in the first three possible areas.

OBJECT:

The purpose of this test was to develop and evaluate a high temperature ceramic adhesive for use in metal to metal bonding. Initial bonding would be made with sheet stock to form a simple lap joint. The ultimate goal of the program was the assembly of honeycomb sandwich specimens suitable for further testing.

CONCLUSION:

Ceramic adhesives will produce a lap-shear strength of over 3000 psi at 800°F. Room temperature lap shear values are not as high as those reached by organic adhesives. Honeycomb panel bonding was achieved but no testing was done.

RECOMMENDATIONS:

Ceramic adhesives offer a definite advantage in high temperature bonding. Being formed at elevated temperatures, they do not burn when resubjected to elevated temperatures. Air vehicles of tomorrow will be operating at temperatures requiring ceramic adhesives. Investigation of ceramic adhesive should be continued so that ultimately a material suitable for production bonding will be available.

1. It is recommended that an attempt be made to duplicate the aluminum porcelain enamel frit, 8102, produced by the Minnesota Mining and Manufacturing Company. Knowing the composition of this glass will help in making modifications.

2. This glass should be subjected to colloidal grinding to lower the initial melting temperature.

3. Additions in controlled sizes should be made of refractory materials. These would offer resistance to the shearing of the adhesive. Additional study is needed in all phases of this program; however, rather than attempt to do everything, the initial study should be made on the three points listed. Answers from these will point out the next phase of study.

TEST SPECIMENS AND PROCEDURES:

The material used for the lap shear tensile testing was 1-1/16" x 4-1/4" x 0.031" 17-7 PH stainless steel. The contact area was reduced to a 1.000" width and the specimens were held so as to produce a lap area of 0.50 square inches with a similar specimen. The details of the lap shear tensile specimen and its firing holder are shown in Figures 1 and 2.

The honeycomb panels were 2" x 2" x 0.500" overall size. The skins were 0.020" and the core was 1/4" hex cell with 0.003" wall thickness. Five panels were made from 17-7 PH core and skins, and five were from PH 15-7 Mo cores and skins.

Specimen Cleaning - Two common methods of metal cleaning prior to the bonding of glass to a metal surface are chemical cleaning and sandblasting. To evaluate the effectiveness of these methods, six lap shear specimens were prepared by each method. The adhesive used was the 1067-1; the temperature was 1750°F and a 50 psi bonding force applied during firing. The samples were tested at 800°F and 1000°F after soaking 10 minutes at heat before pulling.

TEST SPECIMENS AND PROCEDURES: (Continued)

Since chemical cleaning gave the best results, the remainder of the specimens were prepared by this method as shown below:

1. vapor degrease - 3 min.
   tri-chlorethlene degreaser

2. acid etch
   76.0% water
   20.0% nitric acid - concentrated
   4.0% hydrofluoric acid - concentrated
   180-200°F. 0.031" - 10 min;
   0.003" - 3 min.

3. cold running water rinse - 10 min.

4. alkali solution - 180-200°F - 20-30 min.
   oakite cleaner 91 at 6 oz/gal.

5. cold water rinse - 10 min.

Adhesives - Eleven different ceramic frits were formulated, smelted, fritted, ground, and studied in the Lietz Heated State microscope along with a frit formulated by the University of Illinois, and a low melting glass produced by the Minnesota Mining and Manufacturing Co. Formulations for frits C-1 through C-11 will be found in Table I. The batch formulations for these frits and the milling formulas for all adhesives are also found in Table I.

In the remainder of the report the ceramic adhesive frit is referred to by C-, the number indicating the sequence in which the formula was developed, i.e., C-4 was formulated before C-8. When the frit has been prepared into an adhesive it is referred to as C-1-1, C-1-2 and so on. The second number indicates the prepared adhesive is the first, second, or later formulation to be made from that particular ceramic frit. The frit, made by Minnesota Mining and Manufacturing Co., 8102, will be re-referred to as "8102". This glass was developed by the Minnesota Mining and Manufacturing Co. for porcelain enamel on aluminum. This frit has a melting temperature of approximately 1100°F and would be close to the temperature range ultimately desired.

A short explanation of theories controlling the melting temperature of glasses is given in the appendix. The techniques discussed were employed in compounding the formulations made for this work.

TEST SPECIMENS AND PROCEDURES: (Continued)

Heated Stage Microscope Study - After fritting and drying each new batch of adhesive, a heated stage microscope study was made to learn the thermal behavior of the adhesive. The frit was dry ground in a mortar and pestle to pass a 100-mesh screen, (0.0059" openings), and mixed with a few drops of alcohol. The damp frit was hand pressed into a 1/8" cube, dried, placed on a small piece of 17-7 PH 0.010" foil, and observed through a 15X microscope as the temperature was raised. The temperature was allowed to rise at 28°C per min. The observations would stop when the adhesive slumped to a flat shape. The melting temperature referred to in this report is the temperature required to cause the glass frit to pull into a sphere. The flowing temperature is that temperature at which the adhesive slumps to a low mound, losing all identity as a cube or sphere. These conditions are shown in Figures 4 and 5. After cooling, the fused pellet was examined at 60X magnification for corrosive effect on the metal. This provided an opportunity to observe any stress cracking caused by difference in coefficient of expansion.

Furnace Design - To insure good contact between the ends of the lap shear specimens, it was necessary to apply a uniform pressure during firing. None of the existing equipment could be modified. It was necessary to design and construct a furnace with a means of applying the pressure. A sketch of the equipment is shown in Figure 3. By changing the lever arm distances and the variable weight, it is possible to achieve a wide range of pressures on the samples The current was controlled by a variable transformer. A chromel-alumel thermocouple, calibrated to ± 5°F in the temperature ranges used, was located at the bottom of the stack of samples and indicated the temperature through a Leeds and Northrop potentiometer.

Adhesive Slip Preparation, Application and Firing - The adhesive frits selected for tensile testing were ground in water until all particles were less than 0.0017" diameter. See Table I for mill formulations. The milled adhesive slip was adjusted to a specific gravity of approximately 1.6. Ideally all adhesives would have been sprayed at the same specific gravity, but differences in viscosity prohibited this.

The adhesives were applied by spraying a coat that was 0.001" to 0.006" thick after drying. The coating was brushed from the edges of the specimen and the specimens loaded into the firing holder so as to make a lap contact area of 0.50 in. sq. A chromel-alumel thermocouple was inserted in the bottom of the holder. The pressure pad was placed on the stacked specimens, and the entire unit pushed into the furnace. The lever arm was lowered into place on the pressure pad and thus applied a predetermined loading on the lap areas. The temperature was raised as rapidly as possible to the desired temperature and then held for the time considered necessary to cause the adhesive to flow and bond.

The honeycomb panels were fired in a manner very similar to that employed for the lap shear tensile specimens.

TEST SPECIMENS AND PROCEDURES: (Continued)

Lap Shear Testing - The five adhesives selected from the heated stage microscope study, 8102, C-2, C-8, C-10 and C-11 were sprayed on chemically cleaned pieces of 17-7 PH lap shear tensile specimens. Adhesives 8102, C-2, C-8 and C-10 were sprayed on 10 pairs of metal, while the C-11 was sprayed on 5 pairs. The C-2, C-8 and C-10 samples were fired at two temperatures, one near the melting temperature and the other about 200°F higher. The 8102 and C-11 samples were fired at 1050°F. This is near the melting temperature of the 8102 adhesive, and over the maximum temperature needed for the C-11 adhesive.

Mill Additions to Adhesives - Knowing some mill additions improve the bonding of glass to metal, a few tests were made with the addition of various oxides to the adhesives being tested. (1) Four different metal oxides were added to Adhesive UI 1067-1. These were ammonium molybdate, cobalt oxide, nickel oxide, and manganese oxide.

To adhesives C-2-1, C-8-1, C-10-1, C-11-1, and 8102-1 a 10% addition of minus 325 mesh (minus 0.0017") - Fe_2O_3 was made. This new adhesive was sprayed on chemically cleaned 17-7 PH samples as before.

Honeycomb Panels - Table V gives the construction, adhesive, and alloys used in the fabrication of the honeycomb panels.

RESULTS:

Sandblasting vs. Chemical Cleaning - In examining the pieces after testing, it appeared the adhesive bonded more uniformly to the chemically cleaned samples than the sandblasted ones. The adhesive was uniformly divided between the pieces of the lap joint in the chemical cleaning but stuck to one side on the sandblasted pieces. There also appears to be a very definite correlation between a reddish color formed at the interface of the chemically cleaned pieces and the ultimate strength. Within each group, in each temperature range, there is an increase in the lap shear tensile strength as the intensity of the reddish color increases.

Heated Stage Microscope - This instrument revealed differences in melting temperature between the various adhesive frits. These are shown in Figure 6. The information showed the melting and flowing differences developed in the frits because of formulation changes. Frits C-3, C-4, and C-5, modifications of C-2, show little change in melting and flowing temperatures as nickel, silver, and copper are substituted for lithium.

Frit C-6, a modification of UI 1067, has a slightly lower melting temperature than the UI 1067 frit, but surface tension keeps the adhesive together to a much higher temperature before flowing.

RESULTS: (Continued)

Heating Stage Microscope - (continued)

Frits C-7, C-8, C-9, C-10 have zinc and barium introduced at the expense of the sodium. There was little change in the melting temperatures. The 5% Zn added in C-7 lowered the flowing temperature of the C-2 frit approximately 180°C.

Besides indicating melting and flowing temperatures, information as to effect of the adhesive on the metal was also learned by this study. Frits UI 1067 and C-6 have a corrosive action on the metal at the metal-adhesive interface. The other frits did not corrode.

From these frits, five were selected for further study. These were 8102, C-2, C-8, C-10 and C-11. The frit 8102 was selected because it represented a glass with a known low fusion temperature. Frit C-2 was selected as a simple compound with a moderate temperature requirement. The modifications of C-2 found in C-8 and C-10 introduced zinc and barium, as the oxides, respectively. These were melted into the glass to improve the modulus of elasticity. (1) The lead-sodium-silicate frit in formula C-11 was selected after a study of phase diagrams. (12) The 85.2% lead, 10.2% boron, 4.6% silica blend has a low melting eutectic at 473°C.

Lap Shear Testing - The shear values achieved by these adhesives at room temperature and 800°F are given in Table III.

Mill Additions to Adhesives - The results were not as favorable as that achieved by the adhesive alone. See Table IV for listing of values. The difference in values was not considered significant so no further investigation was made. The tensile values obtained by the adhesives with the Fe_2O_3 addition are shown in Table IV. Examples of the specimens after testing are shown in Figure 7.

Honeycomb Panels - The results of the honeycomb panel bonding are shown in Table V.

Some time was spent attempting to determine metallographically what type of bonding existed between the honeycomb, adhesives, and skins. Some bonding is believed to be affected by the "keying" of the adhesive to the chemically roughened surface of the metals. There was some indication of a diffusion zone between the adhesive and the metal, but this was not definite. What other types of bonding might exist cannot be ascertained. Panels 7 and 10 are shown in Figure 8. The filler in the bottom sample is a plastic added to aid in the metallographic polishing.

DISCUSSION:

The simple ceramic adhesive developed by the University of Illinois gave the best lap shear values at room and elevated temperatures. The three component adhesive UI 1067-1 gave average lap shear values of 1350 psi at room temperature and 3070 psi at 1000°F. The other three component adhesive C-2-1 withstood a 970 psi room temperature load and a 1305 psi load at 800°F.

The excellent high temperature strength of the 3M-1082 adhesive is worthy of more investigation. The literature indicates the formulation as an alkali-barium-boron-phosphate glass. Spectrographic analysis lists the main constituents as Na, K, Li, B, Sr and Cd.

The fine values achieved by the UI 1067-1 adhesive may be due to its corrosive action on the metal. This corrosion may be "keying" the adhesive to provide the strong bond achieved. Boron, known to be corrosive to steel, composes 57% of the raw oxide composition and may cause the corrosion. Frits C-6 and C-11 contained 29% and 10.2% boron, but they did not corrode the metal as did the UI 1067 frit.

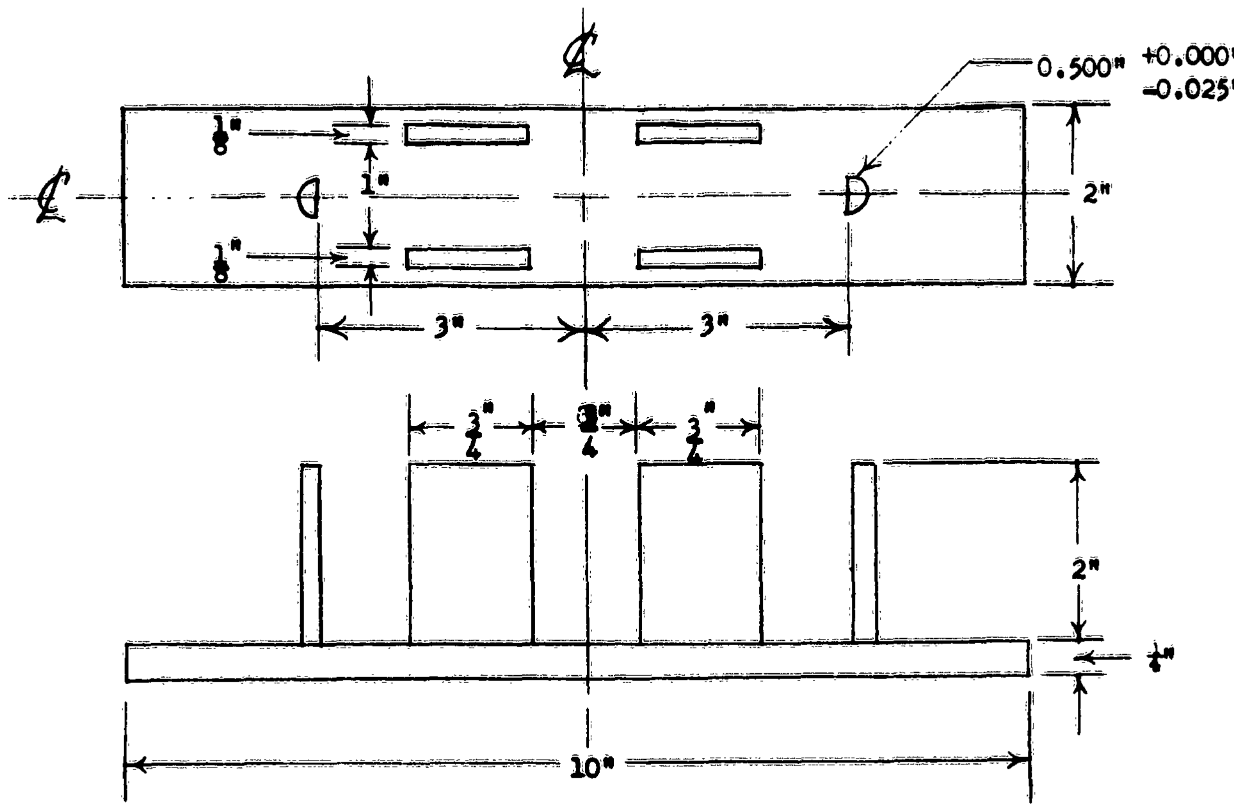
Initially, the corrosion by the UI-1067 frit was not considered desirable and the formulation for the C-2 frit was selected. Lithium is a powerful fluxing agent and along with sodium is able to lower the melting point of silica to 1300°F from approximately 3200°F. No ring of corrosion products is seen with this adhesive or any of its modifications.

The mill additions of cobalt, nickel and manganese oxides adversely affected the strength of the UI 1067-1 adhesive. The 10% addition of minus 0.0017" Fe_2O_3 to adhesives C-2-1, C-8-1, C-10-1, C-11-1, and 3M-8102-1, had an adverse affect on their strength. Whether this adverse affect would be continued if the metals were introduced in another form, i.e., pure metals, is not known.

The lap shear tensile values of the C-2-1 adhesive -

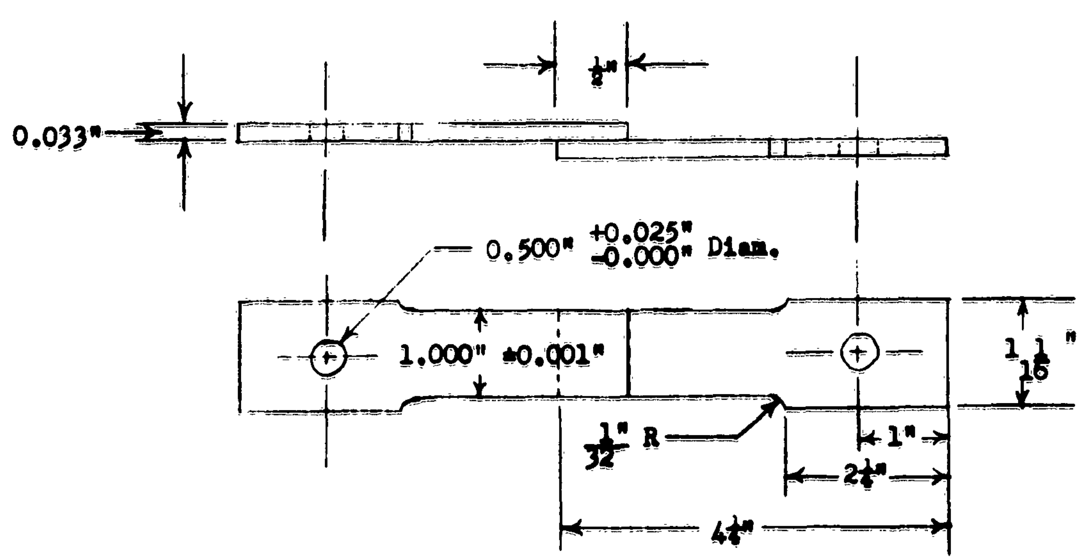
room temperature	970 psi
800°F	1305 psi

are the best of the Convair-developed adhesives. These values are not as good as the UI 1067 adhesive, perhaps because the C-2 does not corrode the metal as does the UI 1067. The values obtained are approximately those first desired, 1000 psi from room temperature to 800°F. These need to be checked in creep, at room and elevated temperatures, sub-zero temperatures, and by other means.



LAP SHEAR TENSILE SPECIMEN FIRING HOLDER

Fig. 2



LAP SHEAR TENSILE SPECIMEN

Fig. 1

METHOD OF APPLYING PRESSURE TO LAP SHEAR SPECIMENS

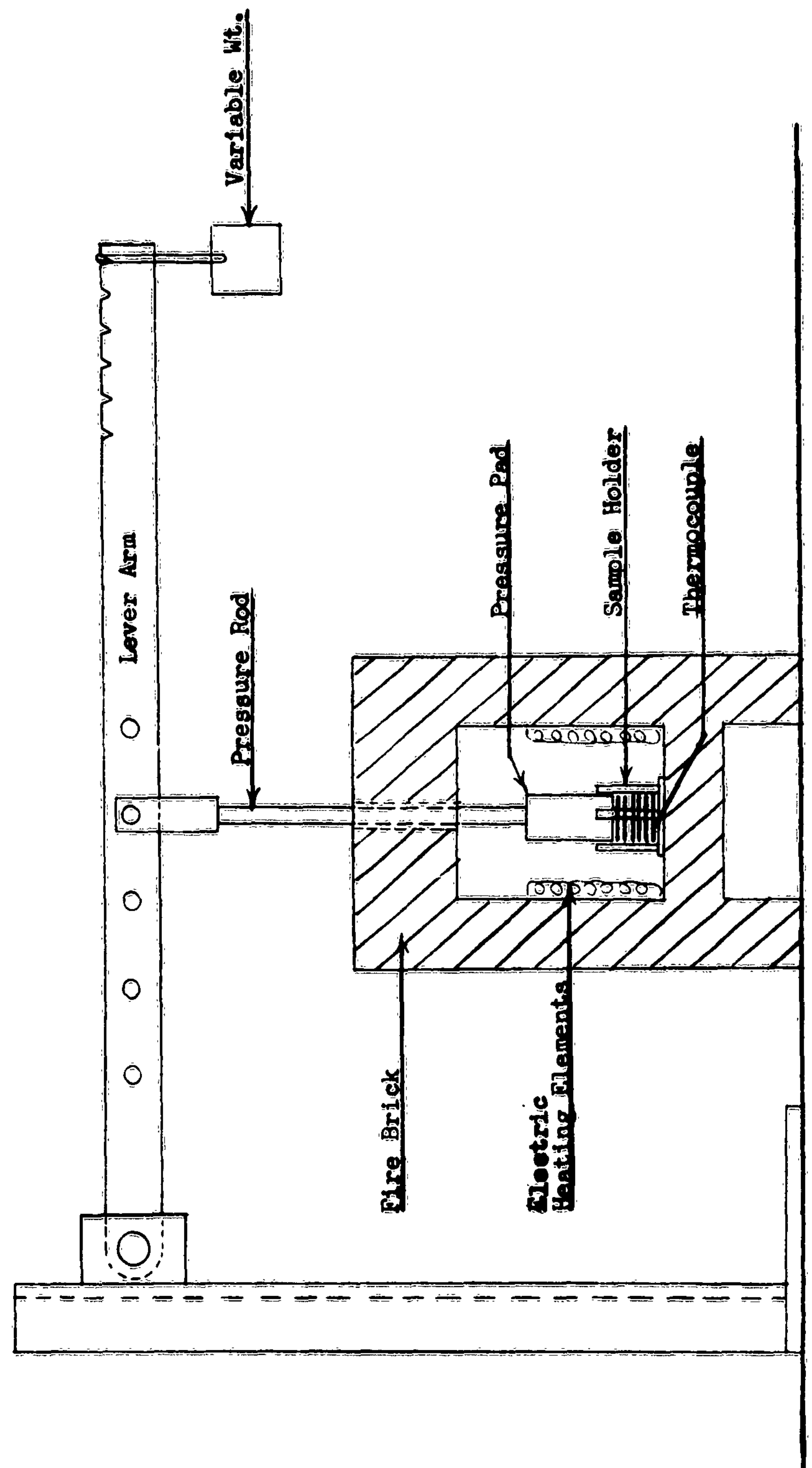


Fig. 3

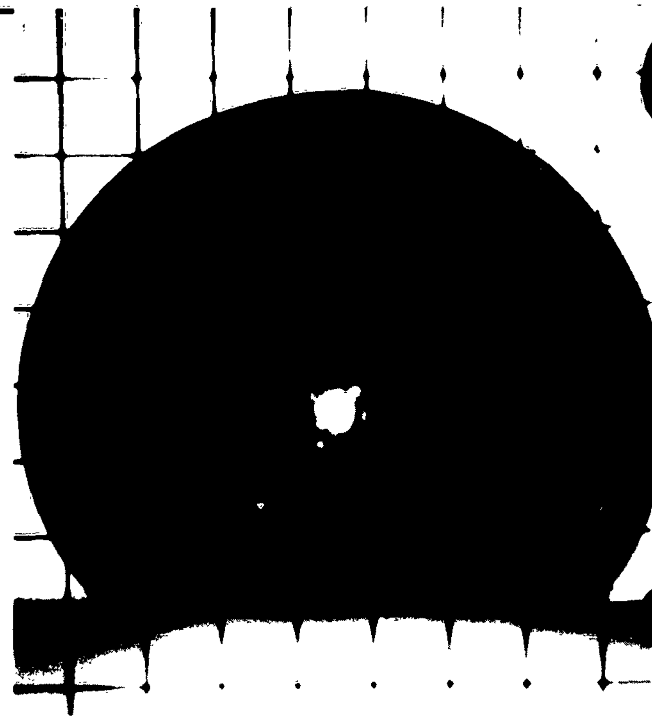
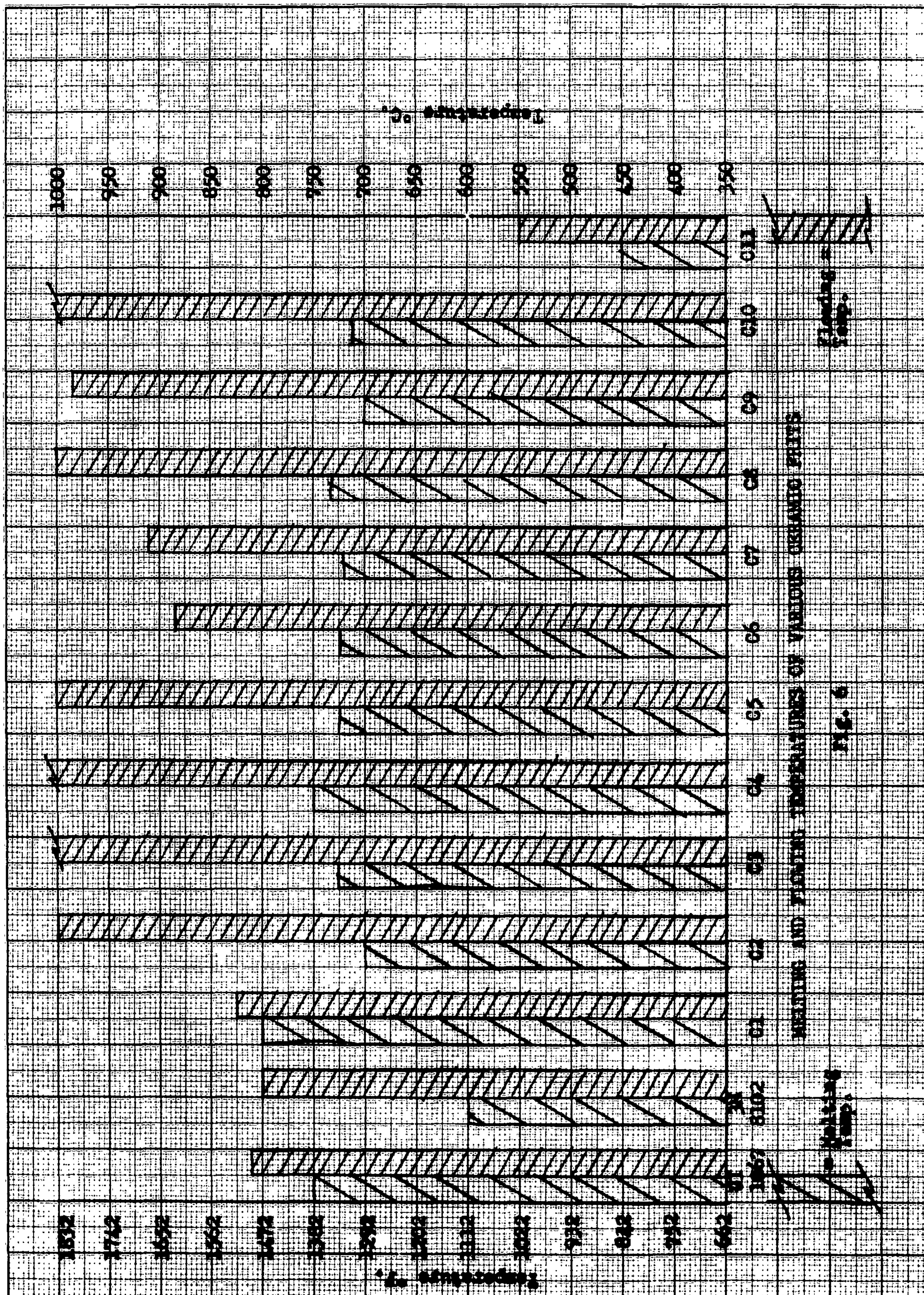


FIGURE 4. CERAMIC FRIT AT ITS MELTING TEMPERATURE

FIGURE 5. CERAMIC FRIT AT ITS FLOWING TEMPERATURE



MELTING AND FLOWING TEMPERATURES OF VARIOUS CERAMIC FRITS

Fig. 6

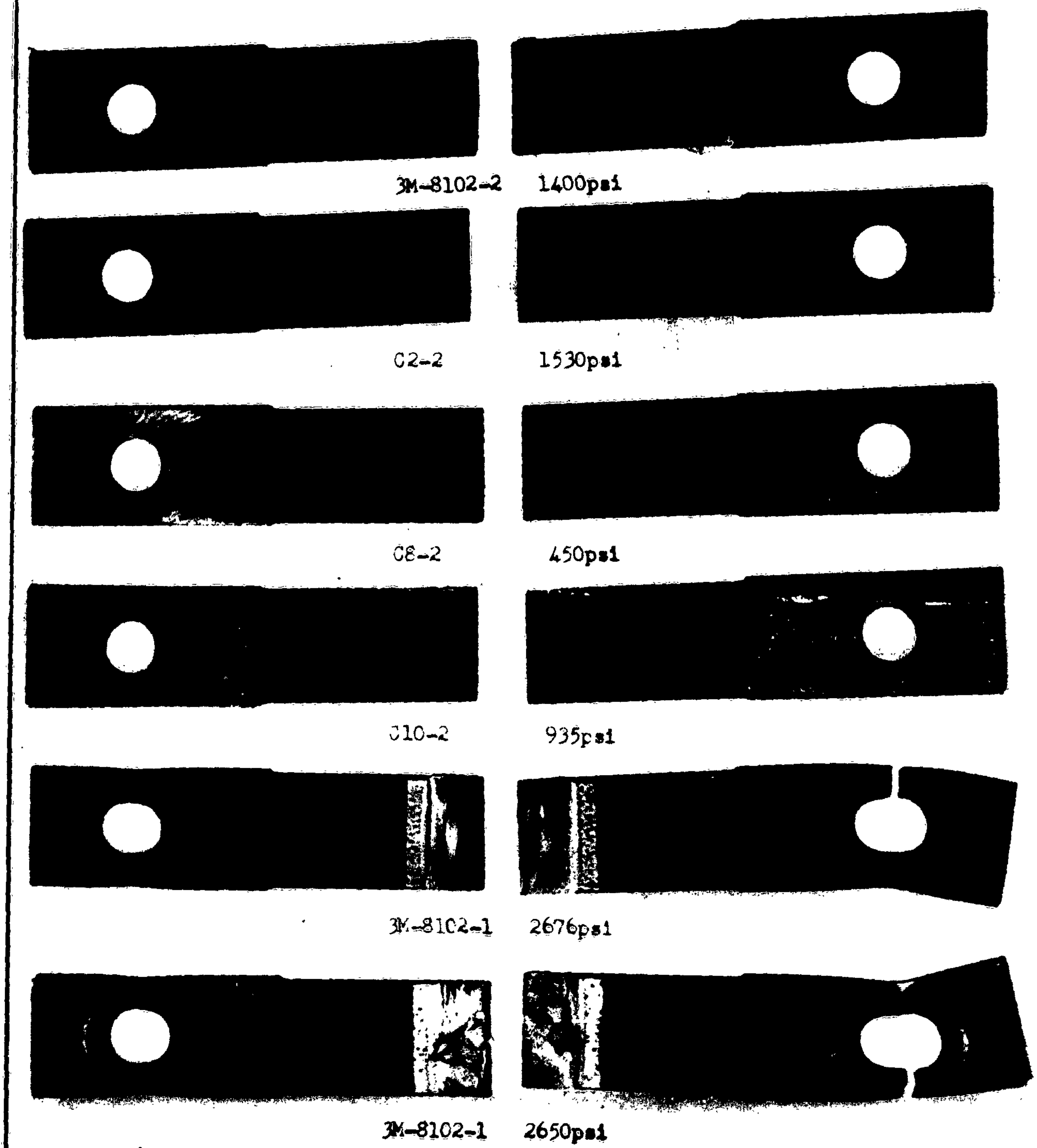
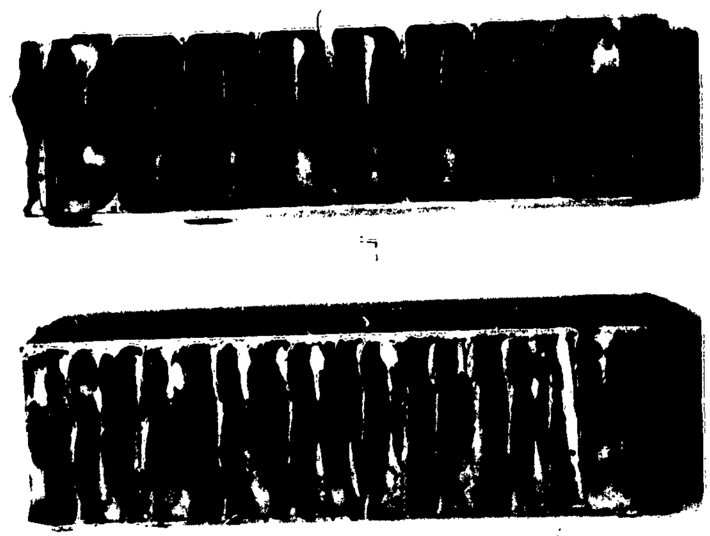


FIGURE 7. VARIOUS LAP SHEAR TENSILE SPECIMENS AFTER TESTING AT 800°F.

FIGURE 8. HONEYCOMB PANELS BONDED WITH CERAMIC ADHESIVES



PH 15-7 Mo SKINS AND CORE BONDED WITH ADHESIVE 3M-8102-1.
BONDING PRESSURE 15 PSI, FUSING TEMPERATURE 1150°F.

PH 15-7 Mo SKINS AND CORE BONDED WITH ADHESIVE C-10-1.
BONDING PRESSURE 15 PSI, FUSING TEMPERATURE 1325°F.

FIGURE 9. FUSION FLOW BLOCK

TABLE I

CERAMIC ADHESIVE COMPOSITIONS

(a) Adhesive Frit Oxide Compositions, Parts by Weight

Oxide	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	UI 1067
SiO_2	26.2	73.0	73.0	70.0	70.0	10.7	73.0	73.0	73.0	73.0	4.6	38.0
Na_2O	20.0	22.0	22.0	22.0	22.0	14.2	17.0	12.0	17.0	12.0	- -	5.0
B_2O_3	9.3	- -	- -	- -	- -	29.0	- -	- -	- -	- -	10.2	57.0
Al_2O_3	13.0	- -	- -	- -	- -	9.8	- -	- -	- -	- -	- -	- -
K_2O	10.0											
CaF_2	5.3											
CoO	7.5											
MnO	1.7											
CoO	5.0											
Li_2O	- -	5.0	2.5	5.0	5.00	- -	5.0	5.0	5.0	5.0		
Ni_2O			2.5	- -	- -							
Ag				3.0	2.75	- -						
CuO	- -	- -	- -	- -	0.25	- -						
	100.0	100.0	100.0	100.0	100.0							
BaO						6.6						
ZnO						6.7	5	10	- -	- -		
MgO						3.3	- -	- -	5	10		
P_2O_5						19.7	- -	- -	- -	- -		
PbO						- -	- -	- -	- -	- -	85.2	
						100.0	100.0	100.0	100.0	100.0	100.0	100.0

TABLE I (Continued

CERAMIC ADHESIVE COMPOSITIONS

(b) Adhesive Frit Raw Batch Formulas, Parts by Weight

Materials	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	UI 1067
Quartz	- -	500	480	498	498	83	532	565	526	555	46	248
$NaNO_3$	56	415	410	430	430	- -	340	260	337	252	102	90
Borax	204					400						662
Alumina	40					76						
Feldspar	355											
CaF_2	60											
Cobalt Oxide	43											
Mn Oxide	14											
Li Carbonate		85	40	44	44		92	97	90	94		
NiCl			70									
Ag Chloride				28	26							
Cu O					2							
BuO												
ZnO						51	36	78				
$MgCO_3$						54						
P_2O_5												
PbO											852	
$BaCO_3$						66			47	99		
$Na_5P_3O_{10}$						265						
Soda Osh	184											
Potassium Carb.	30											
Calcium Carb.	14											

TABLE I (Continued)

CERAMIC ADHESIVE COMPOSITIONS

(c) Ceramic Adhesive Mill Batches

	C-1-1	C-2-1	C-3-1	C-4-1	C-5-1	C-6-1	C-7-1	C-8-1	C-9-1	C-10-1	C-11-1
Frit No.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11
Amount	100	100	100	100	100	100	100	100	100	100	100
Water	40-50	40-50	40-50	40-50	40-50	40-50	40-50	40-50	40-50	40-50	40-50

	UI 1067				
	-1	-A	-B	-C	-D
Frit No.	1067	1067	1067	1067	1067
Amount	100	100	100	100	100
SiO_2	2	2	2	2	2
Water	175	175	175	175	175
NiO	- -	- -	- -	5	5
Co O	- -	- -	5	- -	5
MnO_2	- -	- -	- -	- -	5
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$		0.8			

	-1	-2	3M-8102 C-2-2	C-8-2	C-10-2	C-11-2
Frit No.	8102	8102	C-2	C-8	C-10	C-11
Amount	100	100	100	100	100	100
Mill Agent(2)	XB78	XB78	- -	- -	- -	- -
Amount	15	15	- -	- -	- -	- -
Fe_2O_3	10	10	10	10	10	10
Water	35	35	50	50	50	50

(1) All batches milled til entire batch passed 325M screen (minus 0.0017" or minur 44 microns).

(2) Mill Agent XB78 is a prepared agent to be added to the 8102 frit after grinding. Believe this to be a sodium silicate compound.

TABLE II

LAP SHEAR TENSILE VALUES ACHIEVED BY VARIOUS CLEANING METHODS

Method of Cleaning	Testing Temperature 800°F	1000°F
Chemical	600 psi	3210 psi
	1660 "	2740 "
	1220 "	3260 "
Sandblasting	880 psi	1740 psi
	310 "	1020 "
	1350 "	1400 "

Metal	17-7 PH
Adhesive	UI 1067-1
Firing Temp.	1750°F - Bonding Pressure = 50 psi

TABLE III

LAP SHEAR STRENGTHS OF CERAMIC ADHESIVES

Adhesive	Fired Bond Thickness	Firing Temp. °F	Test Temp. °F	Strength PSI
C-2-1	0.003"	1365	Room	475
	0.001"	1600	Room	970
			800°	1305
C-8-1	0.002"	1365	Room	695
	0.002"	1600	Room	803
			800°	923
C-10-1	0.002"	1365	Room	260
	0.001"	1600	Room	830
			800°	980
C-11-1	0.002"	1150	Room	425
3M-8102-1	0.001"	1150	Room	690
			800°	2665(1)
			800°	[illegible]25(2)
UI 1067	0.001"	1750	Room	1350
			800	1130
			1000	3070

Bonding pressure 25 psi
Samples chemically cleaned
(1) Failed in bearing before failing in shear
(2) Ends reinforced with extra bearing surfaces.

Form 1819

TABLE IV

LAP SHEAR STRENGTHS OF CERAMIC ADHESIVES WITH MILL ADDITIONS

Adhesive	Fired Bond Thickness	Firing Temp.	Test Temp.	Strength PSI	Metal Addition
C-2-2	0.005"	1625	Room	540	10% Fe_2O_3
	0.005"		800	1260	
C-8-2	0.002"	1625	Room	450	
C-10-2	0.006"	1320	Room	740	
			800	865	
C-11-2	0.001"	1175	Room	100	
3M-8102-2	0.005"	1075	Room	577	
			800	1400	
UI 1067	0.002	1750°F	80°F	1130	5% $(NH_4)_6Mo$
UI 1067	0.003	"	"	900	5% CoO
UI 1067	0.003	"	"	1230	5% NiO
UI 1067	0.002	"	"	1050	(5% CoO+ 5% NiO+ 5% MnO)

Bonding pressure = 25 psi
Samples chemically cleaned

TABLE V

HONEYCOMB PANELS: ALLOY, ADHESIVE, AND RESULTS

Panel No.	Alloy	Adhesive	Firing Temp.	Results
1	17-7	C-11-1	1150°F	Failed to bond
2	17-7	C-11-1	1150°F	A heavy application failed to bond
3	17-7	3M-1082-1	1050	Failed to bond
4	17-7	3M-1 on skins C-11-1 on core	1125	Weakly bonded
5	17-7	C-10-1	1625	One skin failed by "peeling" force
6	15-7	C-11-1	1150	Broke apart when sawed in two
7	15-7	3M-1082-1	1125	Firm looking and feeling bond
8	15-7	C-8-1	1350	Firm looking and feeling bond
9	15-7	C-2-1	1400	Firm looking, but broke when pried with fingers
10	15-7	C-10-1	1325	Firm looking and feeling bond

Bonding pressure = 15 psi
Firing time = 5 min. after recovery to firing temperature

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APPENDIX I

DEVELOPMENT OF LOW TEMPERATURE MATURING ENAMELS

INTRODUCTION:

When applying an enamel as an adhesive in the heat treat process (1050°F), a low maturing temperature composition is required. Initial lap-shear tensile tests indicated that non-lead compositions are superior.

THEORY:

A more detailed review of the theories of glass structure has been presented. (2) The basic model is the silica tetrahedron which is linked in a random network and can be changed structurally by the addition of modifiers and other intermediates and network formers.

The practical application of structural consideration is now presented for the development of low melting glasses. (1) Enamels are basically glasses with minor additions for adherence or processing purposes. Changes in composition are governed by the following - - to decrease the maturing point.

(1) Increase the Oxygen Ratio

The lowest oxygen to silica ratio (2:1) occurs in SiO_2 glass and causes a strong, continuous, 3 dimensional network. The addition of one mole of Na_2O to two moles of SiO_2 increases the oxygen ratio to 2.5:1. Examples of change in oxygen ratio are as follow:

Sodium Silicate Glasses	Si	O	Ratio
SiO_2	1	2	2:1
$Na_2O \cdot 2SiO_2$	2	5	2.5:1
$Na_2O \cdot SiO_2$	1	3	3:1
$2Na_2O \cdot SiO_2$	1	4	4:1
Soda-Lime Glasses			
$Na_2O \cdot CaO \cdot 4SiO_2$	4	10	2:5
$Na_2O \cdot CaO \cdot 2SiO_2$	2	6	3:1
$Na_2O \cdot CaO \cdot SiO_2$	1	4	4:1

The oxygen ratio of commercial soda-lime glasses is between 2:1 and 2.5:1. A ratio of 4:1 will not permit glass formation and 3:1 produces weak metasilicate glasses. The modifiers, Na_2O or CaO, increase the oxygen ratio and decrease the melting point. At or above 3:1 oxygen ratio, devitrification occurs more frequently.

THEORY: (Continued)

(2) Use Network Formers of High Valency

The use of phosphates (P_2O_5) glass former, also tetrahedral structure, furnishes an oxygen ratio of 2.5:1 and corresponds to a sodium disilicate glass in ratio. A phosphate glass of the same maturing point as a silicate glass will contain, therefore, less modifier (Na_2O etc.).

(3) Use of a Network Former with Lower Valency

A B_2O_3 glass exhibits a high thermal expansion. When added to silicate composition (amounts to 15 percent) the expansion is lowered by changing to four fold coordination. Above 15 percent the B_2O_3 forms a weak triangular structure and the expansion increases.

(4) Use Monovalent Modifiers

(a) Size of Modifier - The replacement of an alkali ion, with one of smaller size, decreases the maturing point. This effect is explained by the more pronounced weakening of the bonds because of the closeness of an ion of higher positive potential.

Valency	Li	Na	K	Pb	Cs
Radius	.75	1	1.33	1.5	1.75
Potential $\frac{\text{Valency}}{\text{Ratio}}$	1.33	1	0.75	0.66	0.57

This effect however, decreases with increase in alkali ion concentration and can reverse.

(b) Complexity - A mixture of size of ions exhibits a lower melting point than the equivalent single ion composition. The effect is not identical with eutectic or liquidus curves and is more pronounced below the working temperatures.

(5) Change Divalent Modifiers

(a) The prediction of maturing point by the size of the ion is more complex because of the bond of the ion to oxygen.

(b) The complexity effect is the same as for monovalent ions.

THEORY: (Continued)

(6) Use Monovalent Anions (Halogen Ions)

Fluorine can be used to replace part of the oxygen in silicate, phosphate, or borate glasses. The increase $\frac{O + F}{S}$ ratio lowers the maturing point.

4 Na_2O. 12SiO_2	3 Na_2O. 2 NaF .12SiO_2
Ratio 2-4/12:1	Ratio 2-5/12:1

The development of low maturing glasses is at all times limited by devitrification, immiscibility, volatility, and chemical instability.

APPLICATION:

A typical non-lead, low maturing composition is as follows:

Oxide Formula

0.20	Li_2O	0.417	Al_2O_3
0.55	Na_2O	0.208	B_2O_3
0.20	Na_2F_2	0.625	P_2O_5

Ionic Formula

0.40	Li	0.834 Al	5.75 O
0.51	Na	0.416 B	.40 F
		1.250 P	

Corrected Glass Formers to Total 1.00

0.16 Li	0.33 Al	2.30 O
0.70 Na	0.17 B	.16 F
	0.50 P	2.46
	1.00	

The $\frac{O + F}{Former}$ ration = 2.46

Other compositions are found with oxygen to former ratios ranging from 2.11 to 2.98.

APPLICATION: (Continued)

The following investigation was completed to illustrate principles two and three, the use of network formers of higher and lower valencies. Using constant network modifiers (to lower test range) of a percentage normally employed, the percentages of P, Al, and B were varied, as shown in Figure 10, and batches formulated. After smelting, the frits were ground to pass a 100-mesh screen and loaded in the fusion blocks, as shown in Figure 9. The blocks were placed in an electric furnace and the temperature raised slowly until the frits, softened, compacted and the viscosity decreased to a point that flow occurred. The temperature at which the liquid reached the first mark on the block is recorded as the maturing point. The time of flow at constant temperature between the remaining marks affords an indication of the viscosity of the glass. The results of the fusion block tests are also shown in Figure 10.

Three compositions, Figure 11, were evaluated, holding the glass former constant and varying modifier. The areas of low maturing compositions are shown in the above figures.

The above work is presented as a method of approach. Detailed work following this method will yield the low maturing enamels desired subject to other physical and chemical requirements.

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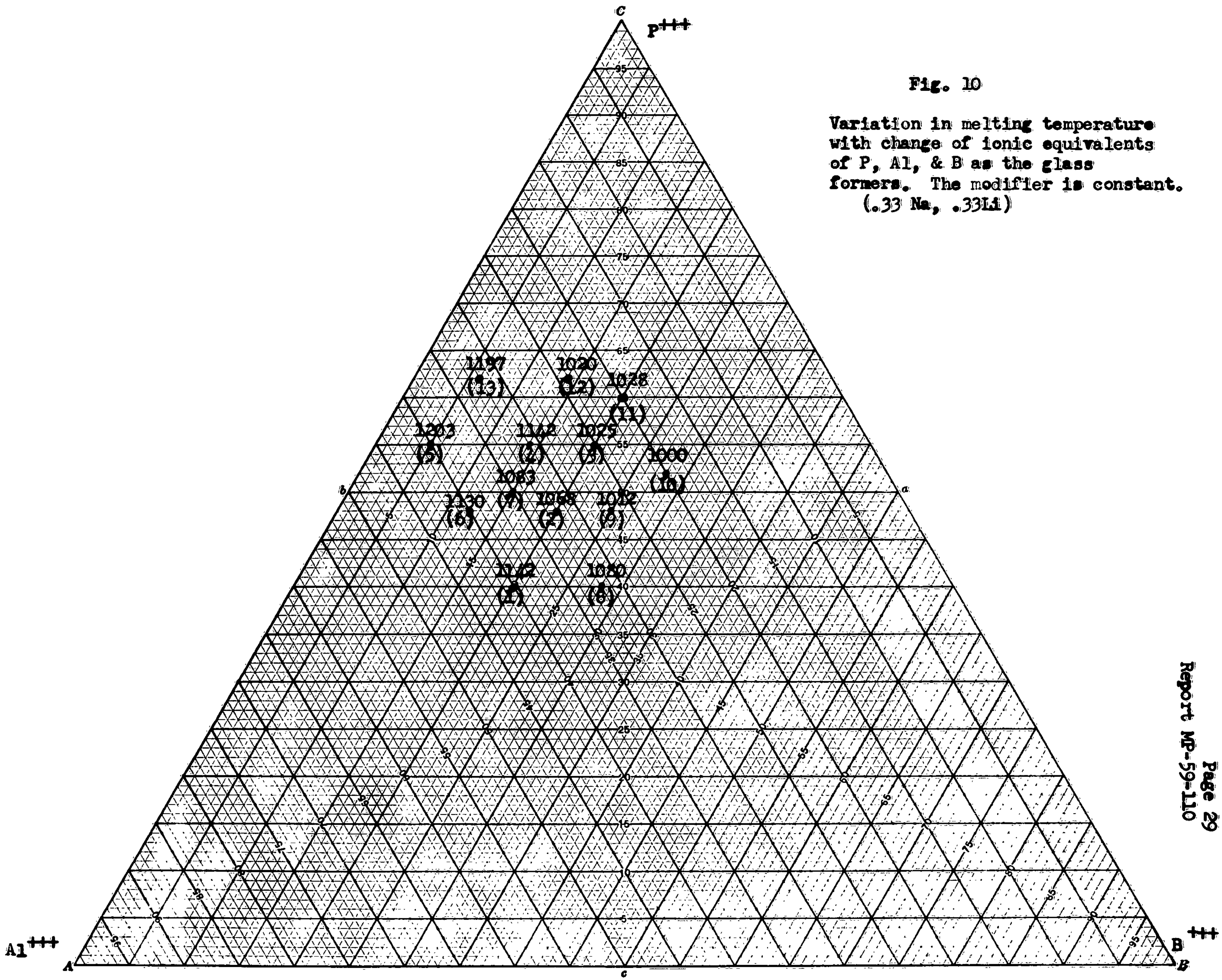

Fig. 10

Variation in melting temperature with change of ionic equivalents of P, Al, & B as the glass formers. The modifier is constant. (.33 Na, .33Li)

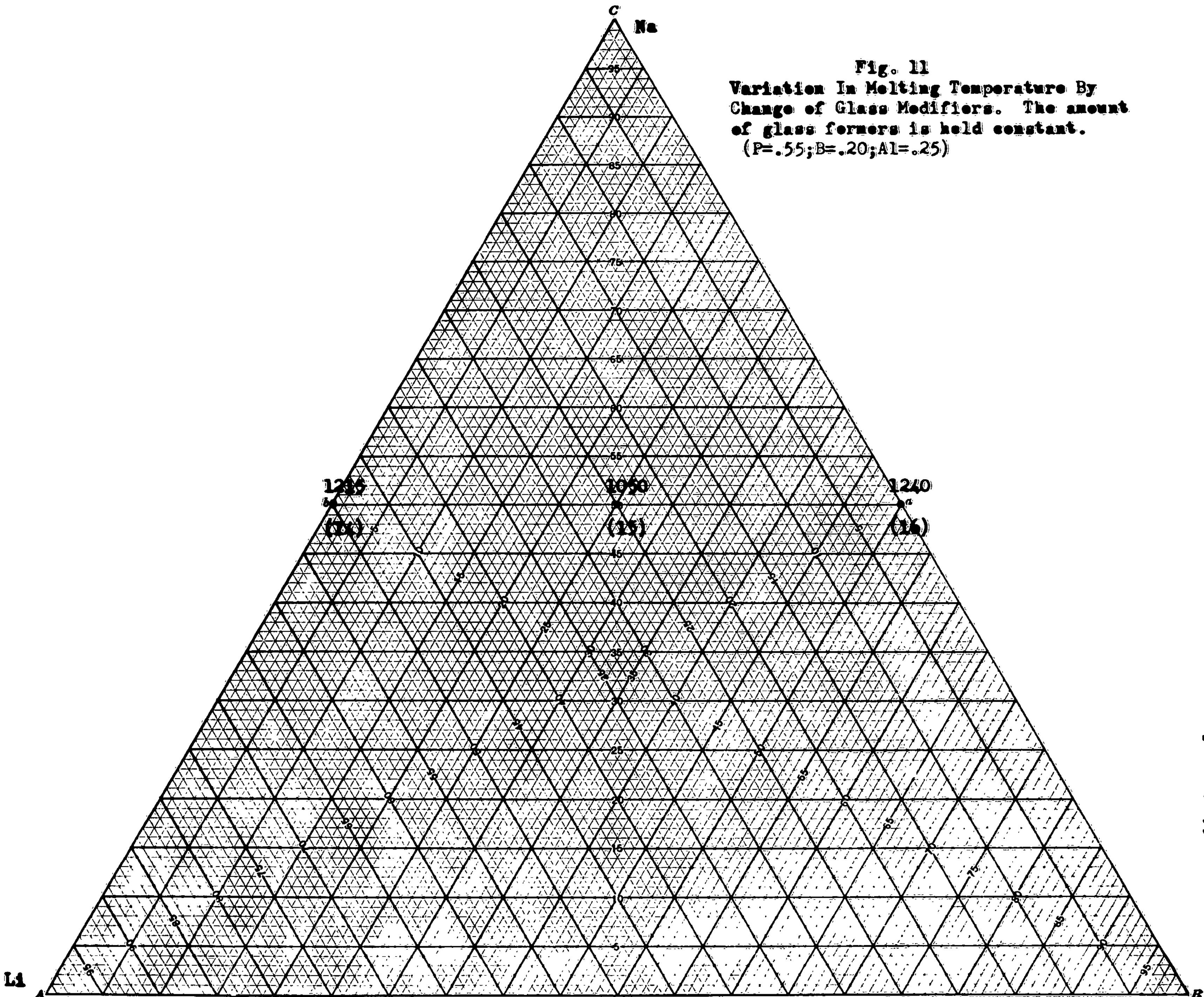

Fig. 11
Variation In Melting Temperature By Change of Glass Modifiers. The amount of glass formers is held constant.
(P=.55;B=.20;Al=.25)